

Patent claims

1. Polymer based on polyazoles whose molecular weight, measured as intrinsic viscosity, is at least 1.3 dl/g*, which can be obtained by a method consisting of the following steps:

- A) mixing of one or more aromatic tetra-amino compounds with one or more aromatic carboxylic acids or their esters, which contain at least two acid groups per carboxylic acid monomers, or mixtures of one or more aromatic and/or heteroaromatic diaminocarboxylic acids;
- B) heating of the mixture, which can be obtained according to step B), under an inert gas, to temperatures of up to 350°C, preferably up to 300°C;
- C) comminution of the mass obtained according to step B) and fractionation of the particles obtained;
- D) heating of the particle fraction of 300 μm to 1000 μm , under an inert gas, to temperatures of up to 450°C, preferably up to 400°C; and cooling.

2. Polymer according to Claim 1, characterized in that the following are used as aromatic tetra-amino compounds: 3,3',4,4'-tetra-aminobiphenyl, 2,3,5,6-tetra-aminopyridine, 1,2,4,5-tetra-aminobenzene, 3,3',4',4'-tetra-aminodiphenylsulfone, 3,3',4',4'-tetra-aminodiphenylether, 3,3',4,4'-tetra-aminobenzophenone, 3,3',4,4'-tetra-aminodiphenylmethane, and 3,3',4,4'-tetra-aminodiphenyldimethylmethane.

3. Polymer according to Claim 1, characterized in that the following are used as aromatic dicarboxylic acids: isophthalic acid, terephthalic acid, phthalic acid, 5-hydroxyisophthalic acid, 4-hydroxyisophthalic acid, 2-hydroxyterephthalic acid, 5-aminoisophthalic acid, 5-N,N-dimethylaminoisophthalic acid, 5-N,N-diethylaminoisophthalic acid, 2,5-dihydroxyterephthalic acid, 2,5-dihydroxyisophthalic acid, 2,3-dihydroxyisophthalic acid, 2,3-dihydroxyphthalic acid, 2,4-dihydroxyphthalic acid, 3,4-dihydroxyphthalic acid, 3-fluorophthalic acid, 5-fluoroisophthalic acid, 2-fluoroterephthalic acid, tetrafluorophthalic acid, tetrafluoroisophthalic acid, tetrafluoroterephthalic acid, 1,4-naphthalenedicarboxylic acid, 1,5-naphthalenedicarboxylic acid, 2,6-naphthalenedicarboxylic acid, 2,7-naphthalenedicarboxylic acid, diphenic acid, 1,8-dihydroxynaphthalene-3,6-dicarboxylic acid, diphenyl ether-4,4'-dicarboxylic acid, benzophenone-4,4'-dicarboxylic acid, diphenylsulfone-4,4'-dicarboxylic acid, biphenyl-4,4'-dicarboxylic acid, 4-trifluoromethylphthalic acid, 2,2-bis(4-carboxyphenyl)hexafluoropropane, 4,4'-stilbenedicarboxylic acid, 4-carboxycinnamic acid, or their C1-20-alkyl esters or C5-C12-aryl

* [sic; molecular weight not usually given in units of dl/g.]

esters, or their acid anhydrides or their acid chlorides.

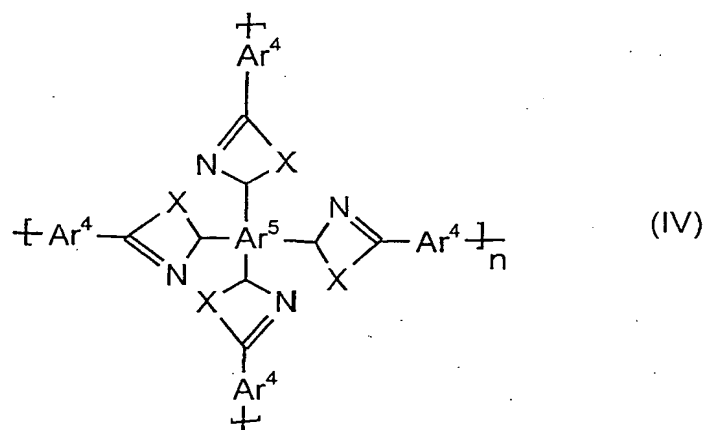
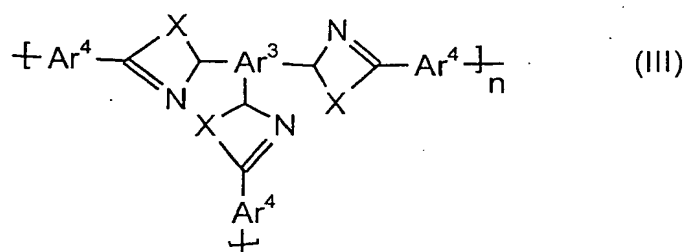
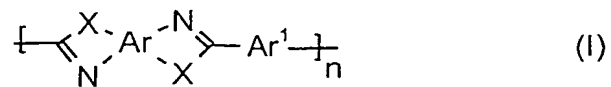
4. Polymer according to Claim 1, characterized in that the following are used as aromatic carboxylic acids: tricarboxylic acids, tetracarboxylic acids, or their C1-C20-alkyl esters or C5-C12-aryl esters or their acid anhydrides or their acid chlorides, preferably 1,3,5-benzenetricarboxylic acid (trimesic acid); 1,2,4-benzenetricarboxylic acid (trimellitic acid); (2-carboxyphenyl)iminodiacetic acid, 3,5,3'-biphenyltricarboxylic acid; 3,5,4'-biphenyltricarboxylic acid, and/or 2,4,6-pyridinetricarboxylic acid.

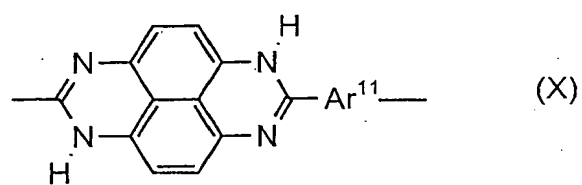
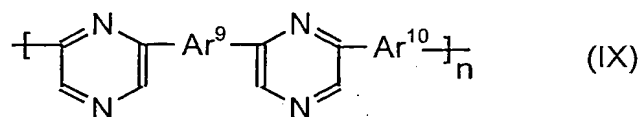
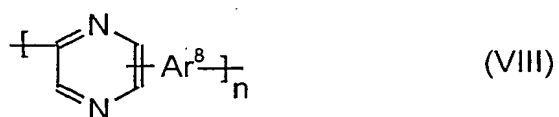
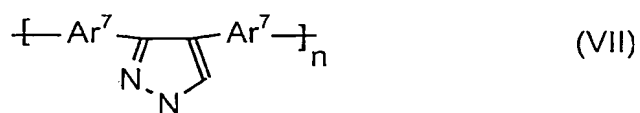
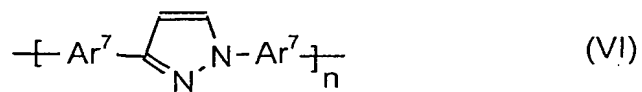
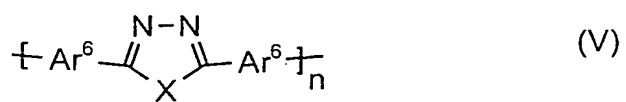
5. Polymer according to Claim 1, characterized in that the following are used as aromatic carboxylic acids: tetracarboxylic acids, their C1-C20-alkyl esters or C5-C12-aryl esters or their acid anhydrides or their acid chlorides, preferably benzene-1,2,4,5-tetracarboxylic acids; naphthalene-1,4,5,8-tetracarboxylic acids, 3,5,3',5'-biphenyltetracarboxylic acid, benzophenonetetracarboxylic acid, 3,3',4,4'-biphenyltetracarboxylic acid, 2,2',3,3'-biphenyltetracarboxylic acid, 1,2,5,6-naphthalenetetracarboxylic acid, or 1,4,5,8-naphthalenetetracarboxylic acid.

6. Polymer according to Claim 4, characterized in that the content of tricarboxylic acid or tetracarboxylic acids (relative to the dicarboxylic acid used) is between 0 and 30 mol%, preferably between 0.1 and 20 mol%, in particular between 0.5 and 10 mol%.

7. Polymer according to Claim 1, characterized in that the following are used as heteroaromatic carboxylic acids: heteroaromatic dicarboxylic acids and tricarboxylic acids and tetracarboxylic acids, which contain at least one nitrogen, oxygen, sulfur, or phosphorous atom in the ring, preferably pyridine-2,5-dicarboxylic acid, pyridine-3,5-dicarboxylic acid, pyridine-2,6-dicarboxylic acid, pyridine-2,4-dicarboxylic acid, 4-phenyl-2,5-pyridinedicarboxylic acid, 3,5-pyrazoledicarboxylic acid, 2,6-pyrimidinedicarboxylic acid, 2,5-pyrazinedicarboxylic acid, 2,4,6-pyridinetricarboxylic acid, benzimidazole-5,6-dicarboxylic acid, and their C1-C20-alkyl esters or C5-C12-aryl esters, or their acid anhydrides or their acid chlorides.

8. Polymer according to Claim 1, characterized in that it contains recurring azole units of general formula (I) and/or (II) and/or (III) and/or (IV) and/or (V) and/or (VI) and/or (VII) and/or (VIII) and/or (IX) and/or (X),





wherein,

Ar are the same or different and [stand] for a tetravalent, aromatic or heteroaromatic group, which can be mononuclear or multinuclear;

Ar¹ are the same or different and [stand] for a divalent aromatic or heteroaromatic group, which can be mononuclear or multinuclear;

Ar² are the same or different and [stand] for a divalent or trivalent aromatic or heteroaromatic group, which can be mononuclear or multinuclear;

Ar³ are the same or different and [stand] for a trivalent aromatic or heteroaromatic group, which can be mononuclear or multinuclear;

Ar⁴ are the same or different and [stand] for a trivalent aromatic or heteroaromatic group, which can be mononuclear or multinuclear;

Ar⁵ are the same or different and [stand] for a tetravalent aromatic or heteroaromatic group, which can be mononuclear or multinuclear;

Ar⁶ are the same or different and [stand] for a divalent aromatic or heteroaromatic group, which can be mononuclear or multinuclear;

Ar⁷ are the same or different and [stand] for a divalent aromatic or heteroaromatic group, which can be mononuclear or multinuclear;

Ar⁸ are the same or different and [stand] for a trivalent aromatic or heteroaromatic group, which can be mononuclear or multinuclear;

Ar⁹ are the same or different and [stand] for a divalent or trivalent or tetravalent aromatic or heteroaromatic group, which can be mononuclear or multinuclear;

Ar¹⁰ are the same or different and [stand] for a divalent or trivalent aromatic or heteroaromatic group, which can be mononuclear or multinuclear;

Ar¹¹ are the same or different and [stand] for a divalent aromatic or heteroaromatic group, which can be mononuclear or multinuclear;

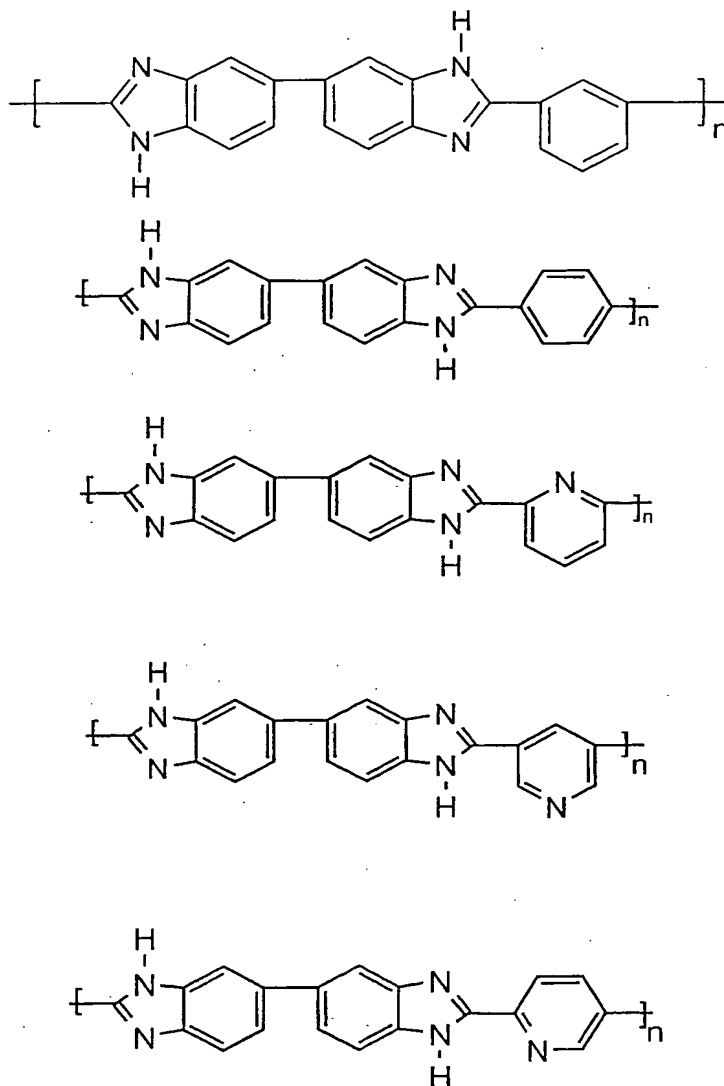
X is the same or different and [stands] for oxygen, sulfur, or an amino group, which carries a hydrogen atom, a group with 1-20 carbon atoms, preferably a branched or nonbranched alkyl or alkoxy group, or an aryl group, as an additional radical; and

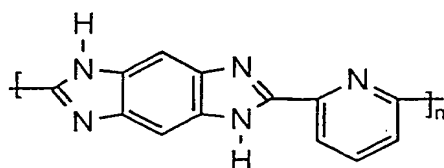
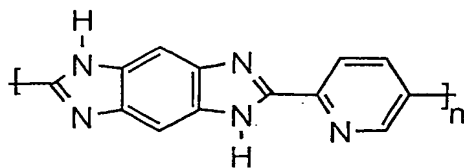
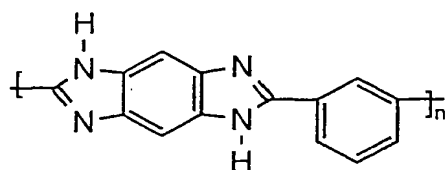
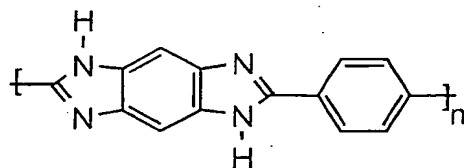
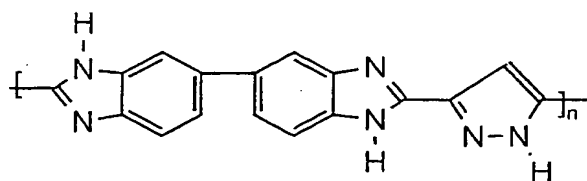
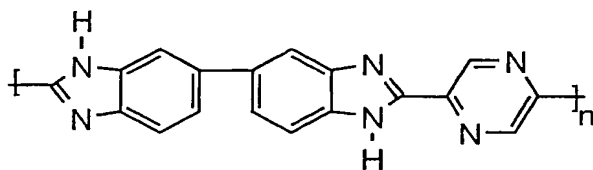
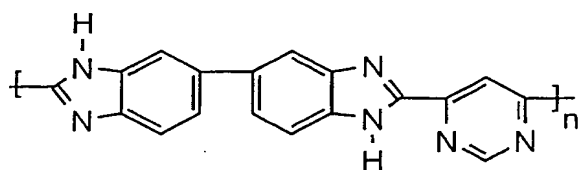
n is a whole number greater than [or] equal to 10, preferably greater than [or] equal to 100.

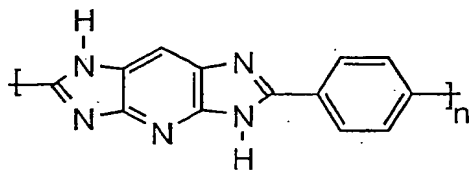
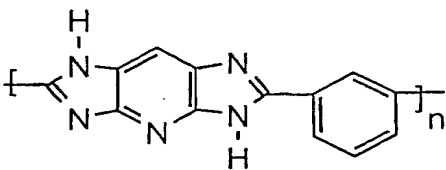
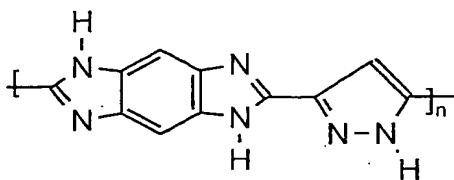
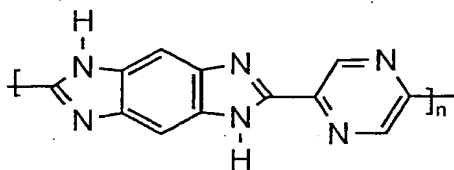
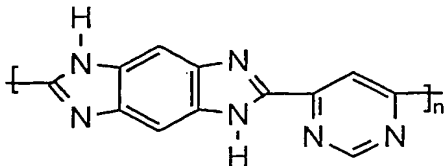
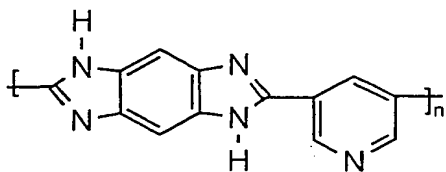
9. Polymer according to Claim 8, characterized in that it is a polymer selected from the group consisting of polybenzimidazole, poly(pyridines), poly(pyrimidines), polyimidazoles, polybenzthiazoles, polybenzoxazoles, polyoxadiazoles, polyquinoxalines, polythiadiazoles, and

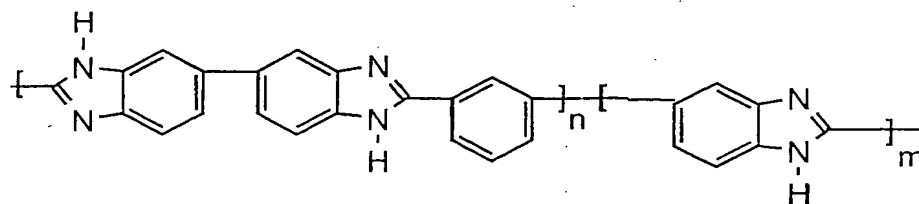
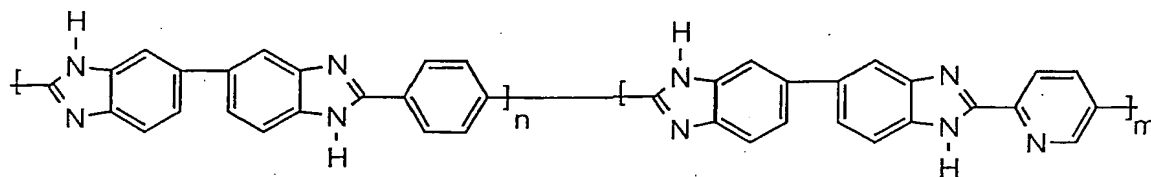
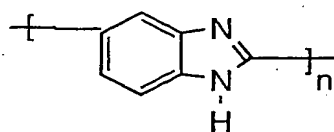
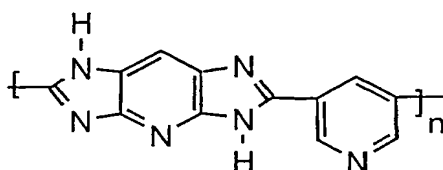
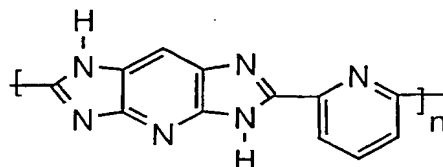
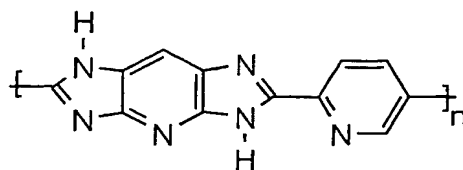
poly(tetrazapyrenes).

10. Polymer according to Claim 1, characterized in that it is a polymer containing recurring benzimidazole units with the following formula:









wherein n and m are whole numbers greater than [or] equal to 10, preferably greater than [or] equal to 100.

11. Polymer according to Claim 1, characterized in that the particle fraction used in step D) contains at least 90 wt% of the particle fraction of 300 μm to 1000 μm .

12. Use of the polymer according to Claim 1 for the preparation of solutions of the

polymer in polar, aprotic solvents, as well as molded articles, films, fibers, and/or coatings.

13. Polymer solutions containing polymers according to Claim 1, dissolved in polar aprotic solvents.

14. Use of the polymer solution according to Claim 13, for the production of molded articles, fibers, films, and/or coatings.

15. Molded article containing at least one polymer according to Claim 1.

16. Fiber containing at least one polymer according to Claim 1.

17. Film containing at least one polymer according to Claim 1.

18. Coating containing at least one polymer according to Claim 1.

19. Use of the film according to Claim 17 in the filtration and/or separation of gases and/or liquids, in reverse osmosis, or for the production of a proton-conducting membrane.

20. Proton-conducting membrane containing at least one polymer according to Claim 1 and at least one doping agent.

21. Use of the membrane according to Claim 20 in electrical condensers, battery systems, in electrolysis, or for the production of a membrane-electrode unit for fuel cells.

22. Membrane-electrode unit containing at least one electrode and at least one proton-conducting membrane according to Claim 20.